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Raman Microprobe Analysis of Stationary Source Particulate Pollutants

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RAMAN MICROPROBE ANALYSIS OF STATIONARY SOURCE PARTICULATE POLLUTANTS

by

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PREFACE

Nearly every aspect of environmental protection involves the identification of specific pollutants. The characterization of the chemical species that comprise individual microparticles is of major importance to the study of their origin and transformation as well as any study of implied health effects. This is especially true in regard to the analysis of combustion particles emitted by stationary sources, such as oil-fired and coal-fired power plants. Raman spectroscopy has evolved as a unique tool for the molecular analysis of microsamples, and the technique is especially suited for the characterization of the chemical species in particulate samples. This report presents the results of the identification and characterization of the major chemical constituents found in single microparticles collected from some oil-fired and coal-fired power plants. Chemical species were identified using the NBS laser Raman microprobe.

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ABSTRACT

The application of Raman spectroscopy to the molecular characterization of individual particles from stationary sources is described. The NBS-developed Raman microprobe has been used to characterize microparticles of oil – and coal – fired power plant emissions and boiler samples collected and described by the Environmental Protection Agency. The samples were examined on an "as received" basis and the results reported do not take into account any sample modifications that may have occured during sample collection.

Vanadium pentoxide, V_2O_5, is identified as a major component of the oil-fired samples. The presence of other vanadium-bearing materials such as sodium metavanadate, $NaVO_3$, and sodium vanadium sulfate, $NaV(SO_4)_2 \cdot 12H_2O$, is indicated. No vanadyl (VO^{2+}) compounds have been detected in these measurements. The laser-induced oxidation of microparticles of vanadyl sulfate to vanadium pentoxide has been observed in controlled microprobe measurements; however, the possibility of such sample modifications having occurred during the analysis of the samples provided is ruled out from experimental considerations. Other Raman spectra are indicative of crystalline sulfates. These sulfates are mostly complex double salts. Materials that have been identified include nickel ammonium sulfate, $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$, iron ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, sodium vanadium sulfate, $NaV(SO_4)_2 \cdot 12H_2O$, calcium sulfate, $CaSO_4 \cdot 2H_2O$ (gypsum), and ammonium sulfate, $(NH_4)_2SO_4$, which we believe to have formed from sulfuric acid upon reaction with ambient ammonia. Raman microprobe analyses of a number of dense agglomerations of largely submicrometer particles, from a sample collected by the EPA and described as coal fly ash, show no Raman spectral features to indicate a glassy material when the particles are first exposed to laser excitation. However, upon continued exposure to laser irradiation the spectral features indicative of a glass developed and may be a result of the thermal transformation of an amorphous material to a fused glass. In many of the spectra obtained from fly ash particles there are Raman features that appear to arise from the presence of carbonaceous materials. These materials may possibly be hydrocarbon residues from the fuel being burned, such as polynuclear aromatic hydrocarbons that are known to be associated with fly ash particles, which are converted to polycrystalline graphite upon exposure to laser irradiation. Recommendations are made as to the scope and further directions of this work.

This report was submitted in fulfillment of contracts EPA-IAG-D7-F1186 and EPA-IAG-78-D-F0367 by the Center for Analytical Chemistry, National Bureau of Standards, under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period August 1, 1977 to July 31, 1979, and work was completed as of July 31, 1979.

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SECTION 1

INTRODUCTION

This report summarizes the work performed under contracts EPA-IAG-D7-F1186, and EPA-IAG-78-D-F0367 covering the period from August 1, 1977 to July 31, 1979. A previous report under contract EPA-IAG-DG-F012, for the period April 1, 1976 to July 31, 1977, presents preliminary results of our initial investigations on stationary source particles (1). The studies reported here are a continuation of this earlier work.

The purpose of this project was to investigate the application of Raman spectroscopy to the determination of the molecular composition of individual, micrometer-size particles in materials collected from stationary sources. The scope of this work entailed activities in the following principal areas:

1. The acquisition and interpretation of Raman spectra of microparticles collected by the Environmental Protection Agency. Materials of interest include oxides, sulfates, nitrates, carbonates, ammonium salts and polycyclic organic matter.

2. The characterization of oil-fired power plant emissions which include the determination of vanadium and sulfur compounds.

3. The characterization of coal-fired fly ash particles.

4. Cooperate with the EPA in developing stack sampling methods (collection, storage, handling) compatible with sample requirements for Raman microprobe analysis.

5. Provide the EPA with a comparison of the capabilities of the NBS Raman microprobe and the Raman microprobe/microscope (MOLE, commercially available from Instruments S. A.) as a tool for the analysis of stationary source particles.

The research conducted under these agreements addresses itself to questions concerning the chemical speciation and crystalline or glassy state of the particles as received from the EPA. A major goal was to further document the potential of Raman spectroscopy as applied to the analysis of the major constituents in particles from stationary sources, with emphasis on those resulting from the combustion of fossil fuels.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results presented demonstrate the potential of micro-Raman analysis for the chemical characterization of particles. Individual particles of size 1 μm and larger can routinely be analyzed. The technique offers good detectability (absolute sensitivity is better than 1 picogram for most scattering species) and speciation of many of the inorganic and organic materials that are of analytical interest in the environment.

Vanadium pentoxide (V_2O_5) has been found as the major component of a large number of particles analyzed in samples from oil-fired power plants. In the majority of these measurements, the Raman spectra unequivocally indicate the oxide of pentavalent vanadium as the predominant vanadium compound in these samples. If any amounts of the lower oxides of vanadium, i.e., V_2O_3 or V_2O_4, coexist in these samples, these would not have been detected as separate species. The two oxides are highly absorbing, opaque materials and, in microprobe measurements, have been shown to convert to V_2O_5 by laser-induced thermal oxidation.

The presence of other vanadium-bearing materials such as sodium metavanadate ($NaVO_3$) is also indicated. Other Raman spectra show evidence for crystalline sulfates. A variety of sulfates have been identified. These are: nickel ammonium sulfate ($Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$), ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), ammonium sulfate [$(NH_4)_2SO_4$, recrystallized from liquids, probably a neutralized sulfuric acid droplet], calcium sulfate ($CaSO_4 \cdot 2H_2O$, gypsum) and sodium vanadium sulfate ($NaV(SO_4)_2 \cdot 12H_2O$, identified principally by indexed electron diffraction patterns and elemental composition). Many of the spectra obtained from the EPA-provided oil-fired fly ash show bands characteristic of polycrystalline carbon. These carbon bands appear to be due to the presence of carboneous materials (organic combustion residues) associated with the particles.

Results from the study of coal-fired fly ash are based on several collections of samples. Many of the samples studied show spectral features characteristic of glasses. One set of samples analyzed did not show Raman features of glass when first exposed to laser irradiation but did show a transformation to the Raman features of glassy (fused) state upon continued exposure to the laser beam. The intensity of the OH-stretching region of the Raman spectrum was observed to decrease during the annealing process indicating that water was being removed from the sample. This sample is probably a hydrated amorphous material which forms a glass upon annealing in the laser beam.

Further work is necessary to fully characterize particulate emissions from power plants. Of special interest is the identification of the hydrated amorphous phase observed in the material described as coal fly ash. This material may be a form of aerosol that is collected in the form of submicrometer samples. A determination of the source of the ammonia observed from many of the particles is also of importance.

In the study of unknown particles a greater emphasis must be placed on the application of other analytical techniques such as electron and ion probe microanalysis to complement the information available through the use of the Raman microprobe. A concerted analysis of the same materials by these techniques may provide a more complete characterization of the particle samples.

SECTION 3

PARTICLE ANALYSIS BY RAMAN SPECTROSCOPY

Raman spectroscopy yields chemical information from the analysis of small, single particles that cannot be obtained through the use of other microanalytical techniques such as electron probe or ion probe microanalysis. The Raman spectrum represents a fingerprint of the constituent chemical species and their structural coordination which readily distinguishes between a broad range of inorganic and organic molecules and also between a variety of crystalline forms of materials that are of the same chemical composition.

The analysis of molecular ions in the atmospheric environment is an area of intense interest and the focus of many current investigations. Of primary importance is an understanding of the chemistry involved in the formation of acid aerosol of which power plant emissions are believed to be a major contributor. This required the determination of the chemical composition of the aerosol and a correlation of this information with particle size.

Raman spectroscopy is, in general, a highly sensitive technique for the identification of the principal components in a sample through the analysis of the molecular vibrations in the sample. We have previously reported the use of the NBS-Raman microprobe for the routine analysis of single particles of size 1 μm and larger. (1-9) These studies demonstrate the broad capabilities of Raman spectroscopy as applied to the analysis of microsamples in many applications. The results of the application of the Raman microprobe to the characterization of emissions from stationary sources is presented in this report.

The Raman spectrum is usually obtained by excitation of the sample in a wavelength region where absorption is minimized. Appreciable absorption of the exciting radiation generally results in sample heating and even modification or destruction. These problems can be particularly severe when high irradiance levels are used. Fluorescence is also a limitation as the fluorescent emission may be intense enough to completely swamp the weak Raman signals. By carefully choosing the laser frequency for excitation, problems of radiation absorption and sample fluorescence can be minimized. Identification and characterization of the molecular compositions of a sample are made by comparing vibrational band patterns of the spectrum to those obtained from either known materials or contained in the literature.

SECTION 4

THE RAMAN MICROPROBE

The Raman microprobe is a conventional Raman spectrometer especially adapted for microanalytical applications. A schematic of the instrument is presented in figure 1 and a detailed description is presented elsewhere (3). An argon/krypton ion laser is used for excitation of the sample. The focused beam can be varied from $\sim$ 2 to 20 μm in diameter on the sample thus giving some control over the intensity (in watts/cm^2) of the beam placed on the sample. The scattered light is collected by an ellipsoidal mirror in a backscattering configuration and then directed into a double monochromator equipped with holographic gratings. The signal is measured with a cooled photomultiplier tube and processed with conventional photon counting electronics. The sample is mounted on a substrate. We commonly use materials such a lithium fluoride (LiF) or sapphire (Al_2O_3) that do not significantly interfere with the measurement. The substrate is mounted on a remotely controlled piezoelectric inchworm translator stage that can reproducibly position the sample in the focused beam. A built-in microscope allows the viewing of the sample for choosing and positioning a particle for measurement. Irradiance levels employed in routine probe measurements range from several hundreds of watts/cm^2 to several mega-watts/cm^2. Measurements times may vary from $\sim$ 15 minutes to several hours depending on the sample being studied.

The Raman microprobe is interfaced to a dedicated minicomputer to permit automatic data acquisition. All instrument functions except control of the laser (i.e., spectrometer drive, slits, chart recorder, photon counting electronics, and sample stage) can be controlled through the interface. The automation has provided a spectral library to be utilized and facilitated data analysis.

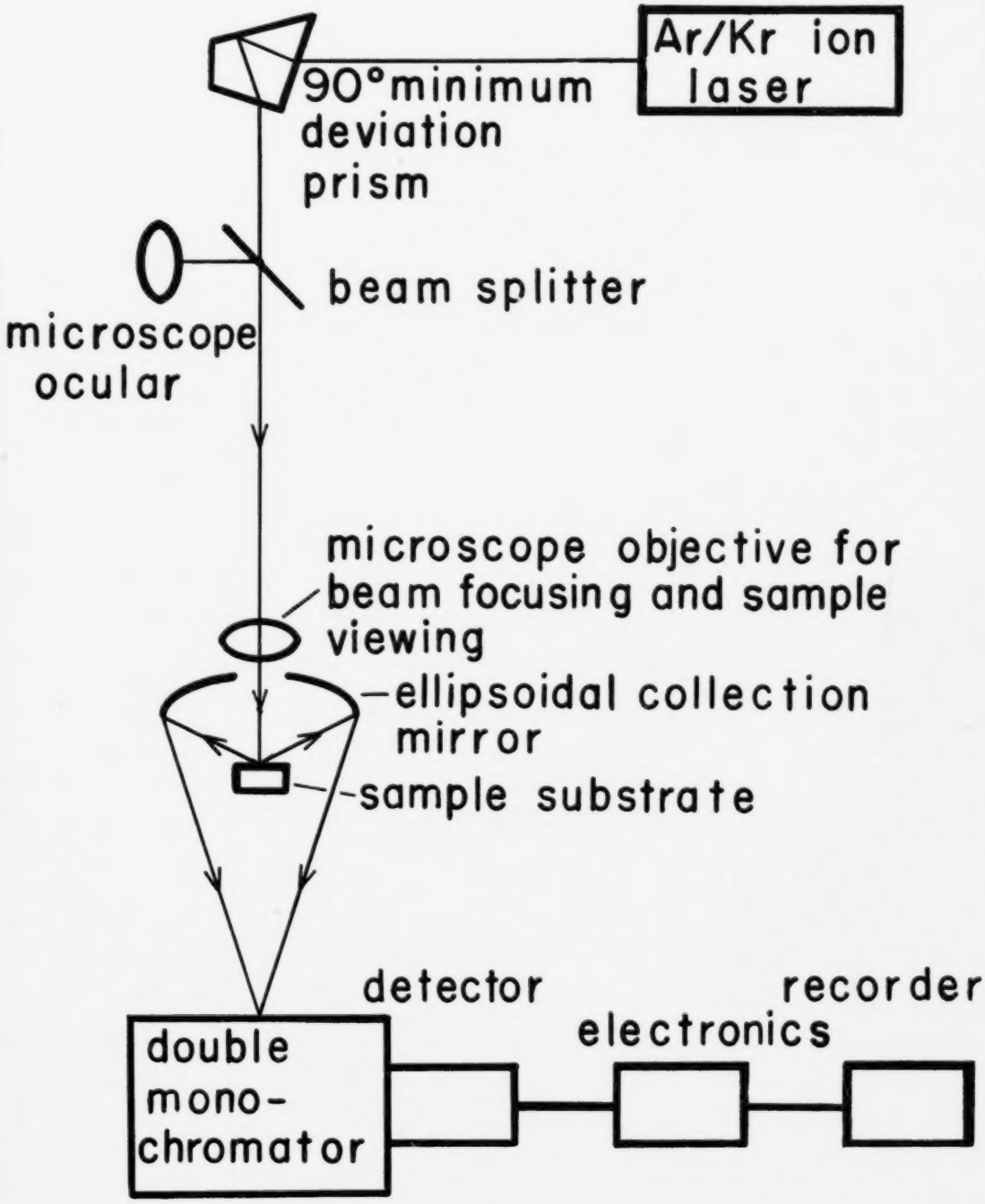


Figure 1. Schematic diagram of the NBS Raman Microprobe.

SECTION 5

CHARACTERIZATION OF UNKNOWN PARTICLES FROM POWER PLANT EMISSIONS

With the emphasis on the control of emissions from stationary sources, there arises a need for more information on the composition of fly ash particles emitted into the atmosphere. Coal- and oil-fired power plants are among the largest anthropogenic point sources of particulate matter.

Limited knowledge is available from bulk samples on the relationship between particle size, distribution and molecular composition in power plant emissions. (10-21) On a particle-to-particle basis there exists little information on the molecular identity of these emissions.(1)

The project objectives include studies on the micro-Raman characterization of particles resulting from the combustion of fossil fuels, with emphasis on identifying the composition of the emissions from oil-fired power plants. The primary interest centers on the identity of the molecular states of oxygenated sulfur and vanadium compounds.

FLY ASH FROM COAL-FIRED POWER PLANTS

Raman microprobe measurements were initially conducted on individual fly ash particles contained in NBS Standard Reference Material, Coal Fly Ash SRM 1633 ("Trace Elements In Coal Fly Ash").(1) The bulk ash is a sieved (< 88 μm) and blended material collected by electrostatic precipitators. Particles ranging in size from ∿ 5 to 20 μm were examined in the Raman microprobe employing high irradiance levels of the 514.5 nm laser beam focused to ∿ 2 μm. The majority of the analyzed particles exhibited weak and diffuse spectral features with a high background so that no characterization could be made. A small number of particles exhibited broad features at ∿ 450 and 950 cm^{-1}. These features are indicative of a glassy structure.(22-25) For a number of larger particles (∿ 10 - 20 μm) which were irregularly shaped, the spectral features indicative of crystalline quartz were found.(26)

Raman microprobe analyses of samples provided by the EPA were first conducted on sample #DPC 15A which was an in-stack, bulk sample of fly ash collected after precipitators and received in the form of a heavy, dense layer of particles deposited on an 80 mm diameter glass fiber filter.(1) A micro-Raman sample was prepared by transferring a light brushing of the ash deposit onto a lithium fluoride substrate. Examination of this preparation in a polarizing light microscope at magnifications from 50 - 625 x showed that the ash consisted of very fine, spherical particles < 2 to 3 μm in diameter with the majority being submicrometer in size and appearing as clusters and long chains. Very few isolated particles were observed.

Individual particles showed little or no birefringence, were fairly transparent in transmitted light and showed various hues of color, mainly brown and green. Spectroscopic measurements were made with 514.5 nm excitation and employing a range of irradiance levels. The lowest irrandiance levels placed on the sample produced heating in the particles. The spectra exhibited high background levels and no observable Raman features. The ash, particles were observed to decompose, melt, and/or vaporize upon exposure to the laser beam. When a larger beam spot (7 - 15 μm) was used, the particles exposed were observed to fuse into larger spheres of globs of solid material. Residue spheres of this type have been produced with diameters 20 - 30 μm. The excessive heating of these particles is attributed to the presence of optically absorbing components in the particles. These may be various colored metal oxides in the matrix or on the surfaces of the particles or films of combustion produced carbon.

Raman microprobe examinations were continued on an "as received" basis with the characterization of several particle samples provided by the EPA and described as coal-fired fly ash. These samples were collected directly onto sapphire substrates with a five stage cascade impactor. These particles were collected in an out-of-stack mode at a point beyond the electrostatic precipitator. Three sets of samples were collected with the second set being collected at significantly shortened sampling times of $\sim$ 1/6 the time of the first collection. Elemental analyses of bulk samples by x-ray fluorescence was conducted by the EPA and the elemental composition was said to be typical of coal fly ash.(11,12,20)

A heavy loading was obtained on the sapphire substrates. These collections were found to be composed of spherical particles < 3 μm in size with the vast majority being below 1 μm when observed in light and electron microscopes. As the loading was heavy, measurements could only be made on agglomerations of particles estimated to be of mass 10 - 50 ng.

By x-ray analysis these particles were principally composed of silicon and aluminum with varying amounts of iron. A number of trace elements were also present. From the appearance of these particles we expected them to heat when subjected to the laser beam and so we analyzed the particles with moderate irradiance levels and repeated the spectral scans to observe any changes that were induced.

Initial examination of one of these agglomerations of particles ($\sim$ 12 μm diameter) in the Raman microprobe showed no prominent spectral features (figure 2a). A repeat scan of this region, while maintaining a constant exposure to the laser irradiance, showed two bands at $\sim$ 735 and 760 cm^{-1} to have developed in the spectrum (figure 2b). No outward evidence of heating (melting of the particle, etc.) was observed, but the Raman spectrum has changed during exposure to the laser beam. Another repeat scan showed that the two features near 750 cm^{-1} are now missing and that two broad features maximizing at $\sim$ 450 and 1100 cm^{-1} are now present in the spectrum (figure 2c). This last spectrum is indicative of a glass.(22-25) No further changes were observed in the spectrum upon continued exposure to the laser beam. The total time of exposure for this area was approximately 100 minutes for each

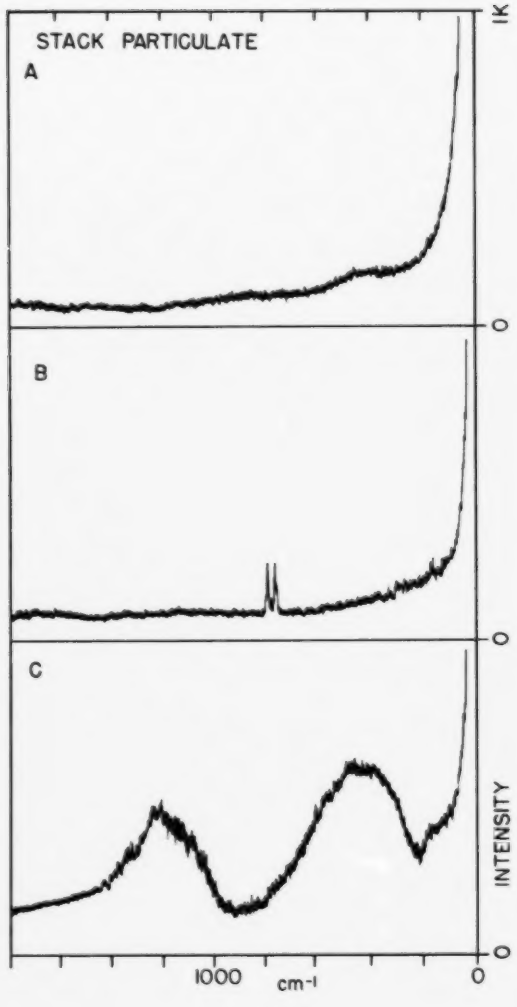


Figure 2. Sequential Raman spectra of an ∿ 12 μm diameter region of a dense particle collection of a coal-fired fly ash. All spectra run at the same conditions: laser; 514.5 nm; power, 50 mW at sample; beam, ∿ 12 μm diameter; spectral slit width, 3 cm^{-1}; time constant, 3.0s; scan rate 0.33 cm^{-1}/s; full scale, 1000 counts.

spectral scan. Other agglomerated areas examined show the same transition from spectra 2a to 2c but only a few exhibited the intermediate spectrum 2b. The areas that showed this intermediate spectrum also had a lower concentration of iron associated with the areas. As iron-bearing compounds can be optically absorbing materials, the decreased concentration of iron in these areas may indicate that the heating experienced may not be as intense so that a slower transition to a glassy state takes place. A decrease in the intensity of the OH-stretching region near 3600 cm^{-1} (not shown) is also observed during the transition to the glassy state indicating that water is being lost.

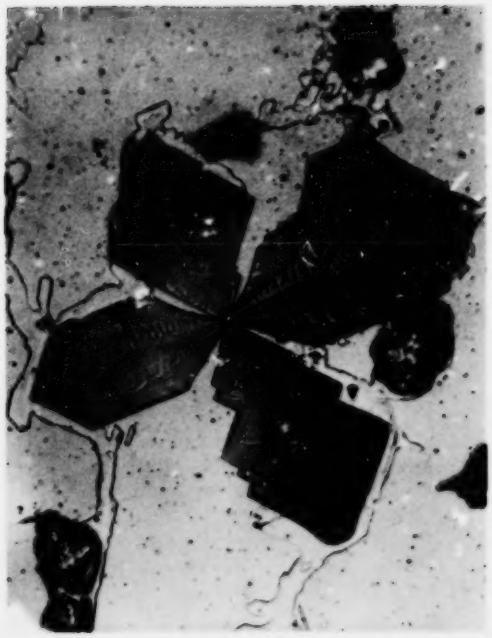
Raman analyses of these agglomerated particles when first exposed to laser irradiation show that the particles are not glass but appear to be an amorphous material that is hydrated. Upon continued exposure of the agglomerated particles to laser irradiation, the particles undergo a transformation to a glassy (fused) state and also show that water is lost from the materials. In some cases an intermediate spectrum is observed with two bands near 750 cm^{-1}. These features are similar to those observed in the spectrum from olivines $(Mg,Fe)_2SiO_4$, which are orthosilicates. (27,28)

These results are at variance with previous investigations of coal fly ash which characterize the particles as being glass. We do not know the exact composition of the amorphous material or what possible modifications have occured during sample collection and further work is needed to determine the exact state of these materials.

PARTICULATE EMISSIONS FROM OIL-FIRED POWER PLANTS

A variety of particle samples from oil-fired power plants have been received from the EPA for analysis in the Raman microprobe. An initial set of five samples was collected from a power plant labelled Site A and a preliminary report of our analyses has been made.(1) Representative of some of these particles are those seen in figure 3. Measurements on these particles have been continued during this work period and additional results are described in this report.

Our measurements on particles from the fourth impaction stage have furnished a number of essentially identical Raman spectra for the dendritic microcrystals. Representative of these spectra is that shown in figure 4, obtained from probing a small segment of the large four-leaved crystal seen in figure 3a. The predominant bands in these spectra are located at $\sim$ 145, 280 and 1000 cm^{-1}. The major constituent present in these particles is crystalline vanadium pentoxide, V_2O_5. The Raman spectrum of V_2O_5 has been discussed in the literature (29) and corroborating spectra have been obtained from well characterized samples of V_2O_5. Besides the features of V_2O_5 (104, 144, 285, 406, 701 and 995 cm^{-1}), there exist additional bands of medium intensity in the region 820 to 970 cm^{-1} which are absent in the spectrum of pure V_2O_5. These bands are similar to those of both VO_3^- (metavanadate) and VO_4^{3-} (orthovanadate) ions (30,31); however, the exact compounds have not been identified.



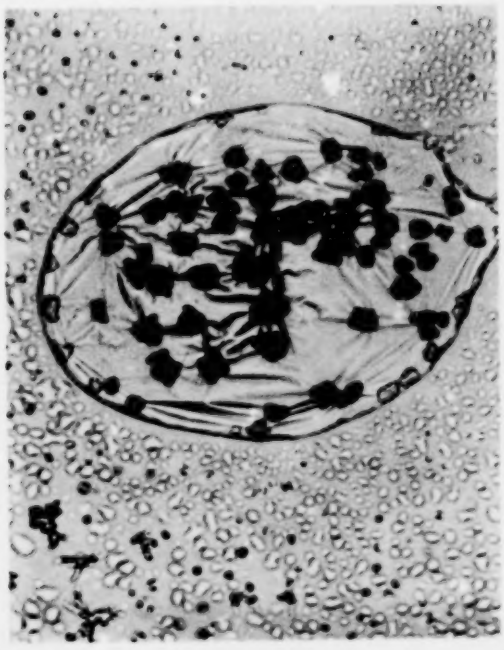


Figure 3. Optical micrographs of oil-fired power plant stack particles collected on sapphire substrates. Magnification 312 x.

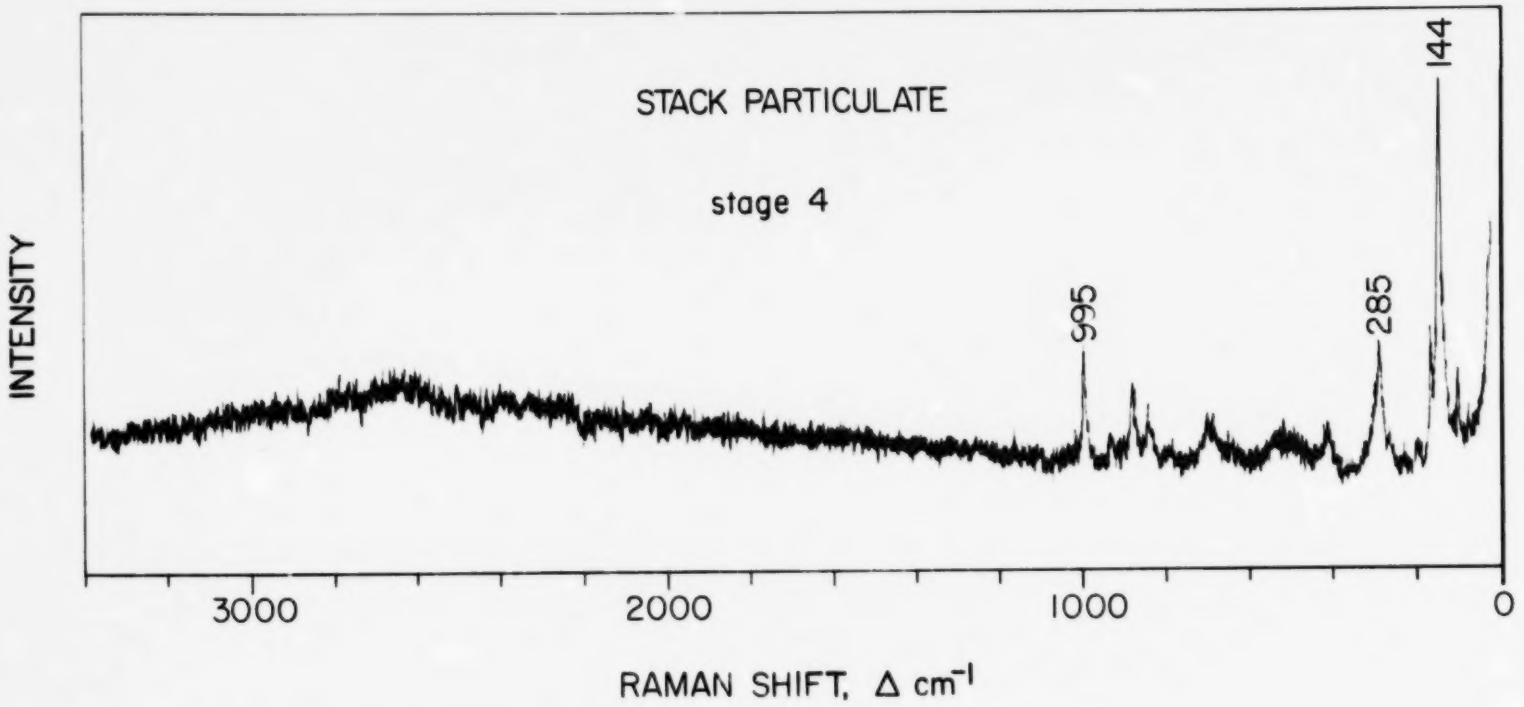


Figure 4. Raman spectrum recorded from probing a small region of the large four-leaved particle shown in figure 3. Substrate, Al_2O_3; laser, 514.5 nm; power, 60 mW at sample; beam, 6 μm diameter; spectral slit width, 3 cm^{-1}; time constant, 0.8s; scan rate, 0.83 cm^{-1}/s; full scale, 1000 counts.

Raman spectra obtained from the globular particles presented in figure 2 are indicative of a crystalline sulfate. Representative of these spectra is that shown in figure 5. Four distinct band groups are seen with the most intense band maximizing at $\sim$ 980 cm^{-1}. This band appears split with the second component at $\sim$ 990 cm^{-1}. The lower frequency bands are centered around 625, 460 and 150 cm^{-1}. The spectral features at 981, 625 and 460 cm^{-1} are indicative of crystalline sulfates and, in this case, a hydrated metal ammonium sulfate.(32-34) The major component of this particle is identified as nickel ammonium sulfate $(Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The other two features at $\sim$ 990 and 150 cm^{-1} are identified with V_2O_5. These last two bands have been observed to be produced by irradiance induced heating of the sample and may arise from the presence of other vanadium compounds such as V_2O_4 or V_2O_3 which convert to V_2O_5 when exposed to the laser beam. In figure 6, we present a series of three sequential spectra taken from one of these globular particles. Initially a low irradiance level was used and the resulting spectrum (top) shows a large background, the spectral features of nickel ammonium sulfate and carbon bands maximizing at $\sim$ 1350 and 1600 cm^{-1}. These carbon bands are characteristic of elemental carbon in a polycrystalline form and have been found to be produced by the thermal decomposition of residual carbonaceous materials associated with the particulate sample. (6) Upon exposure of the particle to a higher irradiance (middle), we can observe that the two bands at $\sim$ 144 and 990 cm^{-1} are now present together with the features of nickel ammonium sulfate and the carbon bands. The high background is still present. A repeat scan utilizing the lower irradiance conditions (bottom) shows the bands of nickel ammonium sulfate and vanadium pentoxide. The background has been reduced and the carbon bands are not observed in the background. No spectral indications for the presence of vanadyl sulfate are found in the initial low irradiance spectrum. As vanadyl sulfate is stable under the low irradiance conditions used in this demonstration, its presence would be deduced by the observation of the major Raman bands (1071, 1027, 1003, 645, 480, 468, 321, 276, 253, 213, 159, 123, 99, and 66 cm^{-1}) characteristic of that compound (5). None of the spectra obtained from oil ash particle analyzed in this work have allowed us to postulate the presence of $VOSO_4$ in these samples.

Similar spectra were obtained from particles on the third impaction stage. In addition to vanadium pentoxide and nickel ammonium sulfate, we also found iron ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and calcium sulfate ($CaSO_4 \cdot 2H_2O$), gypsum (35,36) (figure 7) to be present. The iron ammonium sulfate was found in particles that appeared to be morphologically similar to those of nickel ammonium sulfate. The gypsum was found only in a few large particles located on the stage.

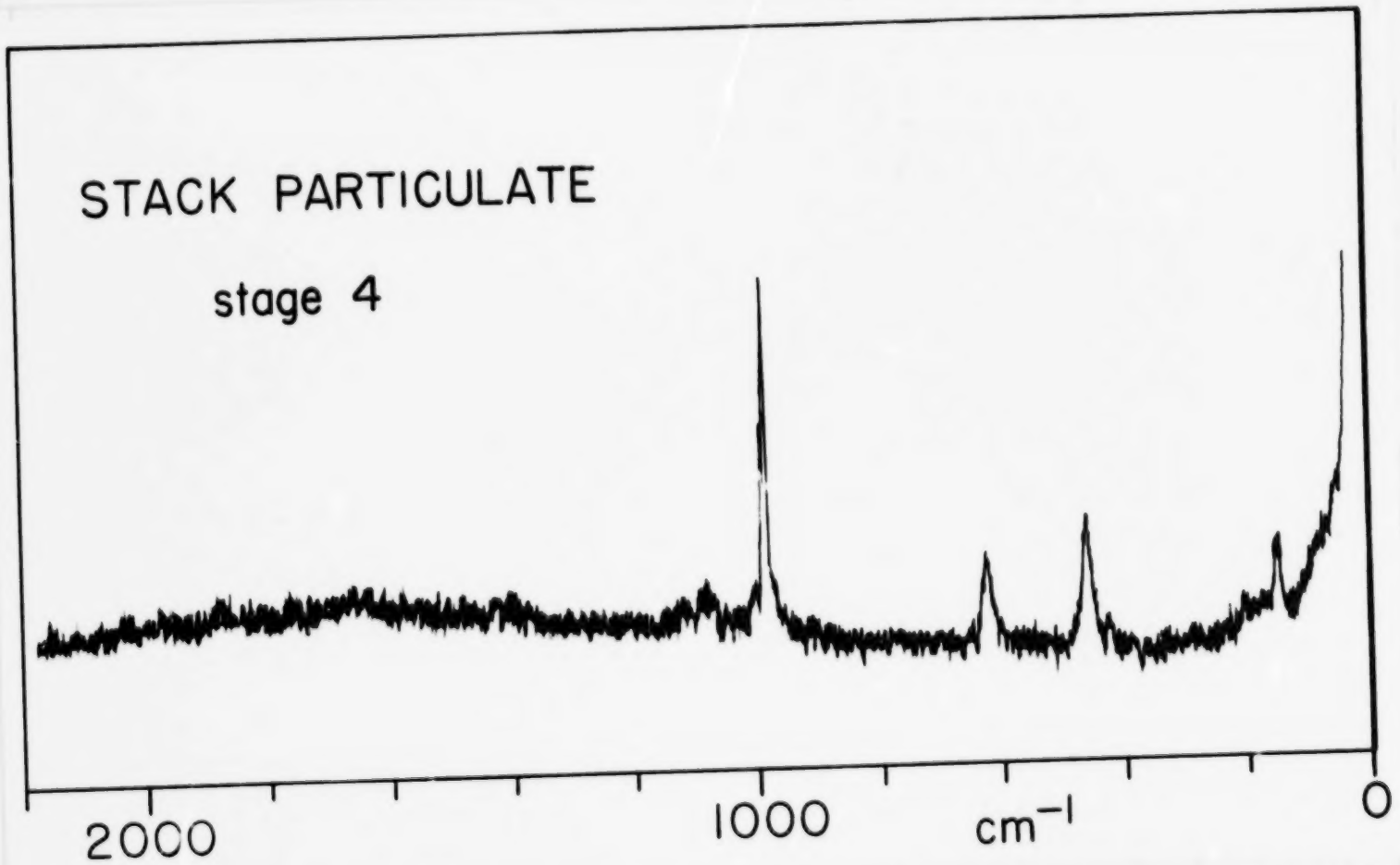


Figure 5. Raman spectrum of a globular particle found on stage 4, identified as nickel ammonium sulfate. Particle, 7 x 9 μm; substrate, Al_2O_3; laser, 514.5 nm; power, 20 mW at sample; beam, 20 μm diameter; spectral slit width, 3 cm^{-1}; time constant, 1.0s; scan rate, 0.83 cm^{-1}/s; full scale, 1000 counts.

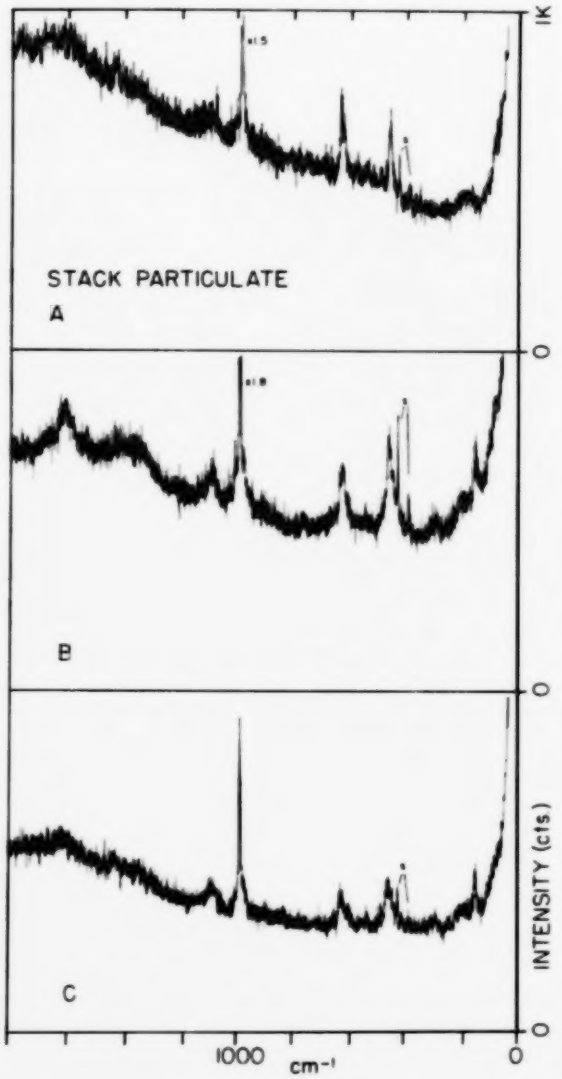


Figure 6. Raman microprobe spectra of a stack particle from an oil-fired power plant illustrating laser-induced sample changes. Particle, 8 x 12 μm; substrate, Al_2O_3; laser 514.5 nm; spectral slit width, 3 cm^{-1}; scattered intensity, 1000 counts full scale. Parameters varied: power (at sample), 25 mW [A,C], 120 mW, [B]; beam spot, ∿ 18 μm [A,C], ∿ 8 μm [B]; time constant, 3.0s [A,C], 1.0s [B]; scan rate, 0.33 cm^{-1}/s [A,C], 0.83 cm^{-1}/s [B]. Bands marked s arise from scattering by the sapphire substrate.

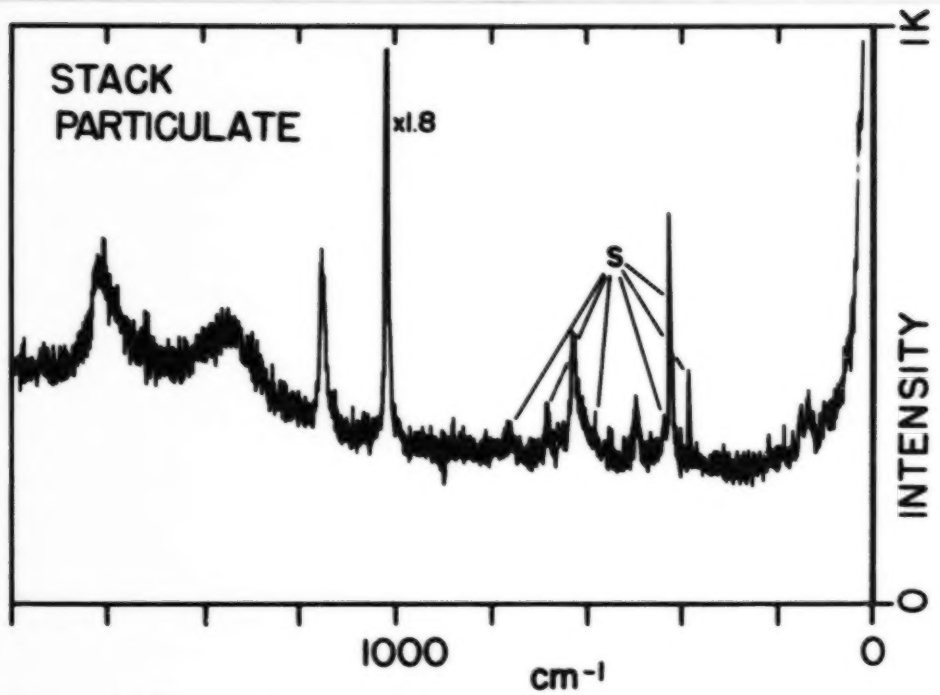


Figure 7. Raman spectrum of a large gypsum particle found on stage 3. Particle, ~ 15 x 60 μm; substrate, Al_2O_3; laser 514.5 nm; power, 120 mW at sample, beam, ~ 8 μm diameter; spectral slit width, 3 cm^{-1}; time constant, 1.0s; scan rate, 0.83 cm^{-1}/s; full scale, 1000 counts.

It was concluded from light microscop observations that the particles on stage 5 may, at the time of collection, have been liquid droplets. When we placed this sample into the Raman microprobe for analysis we found that the droplets had crystallized and thus we were not able to analyze the liquid material. A Raman spectrum from one of these crystallized particles is presented in figure 8. This has been identified as ammonium sulfate, $(NH_4)_2 SO_4$, and is probably the result of neutralization of an acid droplet with ambient ammonia.

A set of boiler scale samples, one each taken from what is described as the oxidizing and reducing sections of the boiler, have been collected from an oil-fired boiler by the EPA and submitted for Raman microprobe analysis. It was hoped that the analysis of these samples might give some insight into the composition of the chemical species formed in the combustion zone.

Light microscopic examination of these particles showed them to be coarsely granular chunks of heterogeneous material with colors ranging from yellow-green and yellow to brown and black. These materials were also observed to be hygroscopic. To perform Raman analysis, small particles that appeared reasonably homogeneous were isolated and mounted on sapphire substrates for examination in the Raman microprobe.

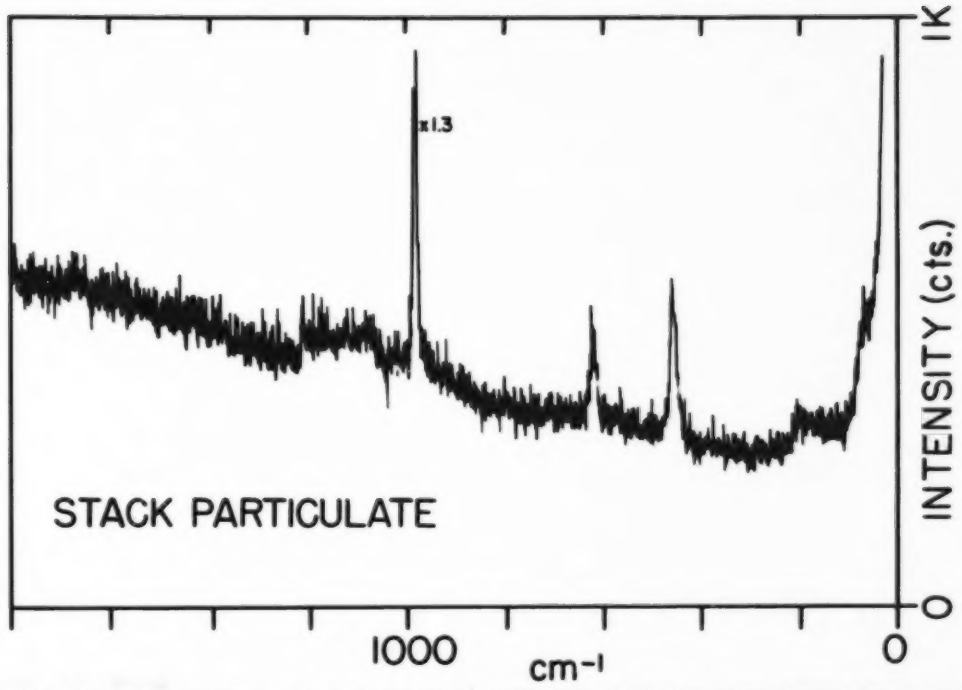


Figure 8. Raman spectrum of a recrystallized liquid droplet found on stage 5. The material is ammonium sulfate. Particle, ~ 10 x 16 μm; laser 514.5 nm; beam 18 μm diameter; power, 25 mW at sample; substrate, Al_2O_3; spectral slit width, 3 cm^{-1}; time constant, 1.0s, scan rate 0.83 cm^{-1}/s, full scale, 1000 counts.

Particles analyzed from the sample labelled oxidizing section gave Raman spectra indicative of vanadium pentoxide, V_2O_5, nickel ammonium sulfate, $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and iron ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, which was present only in a few particles. No heating was observed in these particles and no evidence for carbon associated with these particles was found.

The same materials that were found in the sample labelled oxidizing section were found in the sample labelled reducing section. In addition two other types of spectra were found. Figure 9 is a presentation of one of these spectra which have been observed from a number of particles. This spectrum has been identified, by comparison to the spectrum of a laboratory-prepared sample, to be that of sodium metavanadate, $NaVO_3$. The second

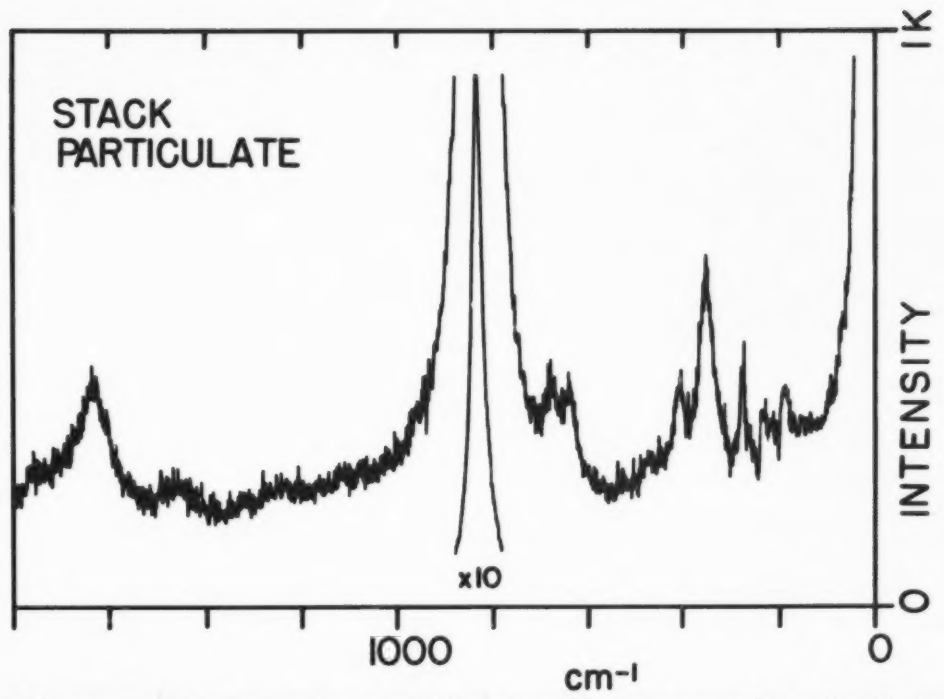


Figure 9. Raman spectrum of a particle of sodium metavanadate found in on oil-fired power plant. Particle ∿ 14 x 18 μm, laser, 514.5 nm; power 5 mW at sample, beam ∿ 12 μm diameter; substrate, Al_2O_3; spectral slit width, 3 cm^{-1}; time constant, 6.0s; scan rate, 0.16 cm^{-1}/s; full scale, 1000 counts.

spectrum (figure 10) has been observed from a small number of particles. We have not as yet been able to identify this spectrum by comparison to literature or to the spectra of known materials. Elemental analysis by energy dispersive x-ray analysis showed only Na, V and S to be the major elements present. There were also trace amounts of Ca, K, Ni and Fe present. Individual particles were analyzed by electron diffraction and on the basis of the indexed patterns and elemental composition, these particles can be tentatively identified as sodium vanadium sulfate, $NaV(SO_4)_2 \cdot 12H_2O$. However, we have not been able to obtain a Raman spectrum of laboratory-prepared sodium vanadium sulfate to positively identify the Raman spectrum. The spectral features associated with polycrystalline graphite have also been found in some of the Raman spectra obtained from this sample; however, no evidence of extensive heating was observed.

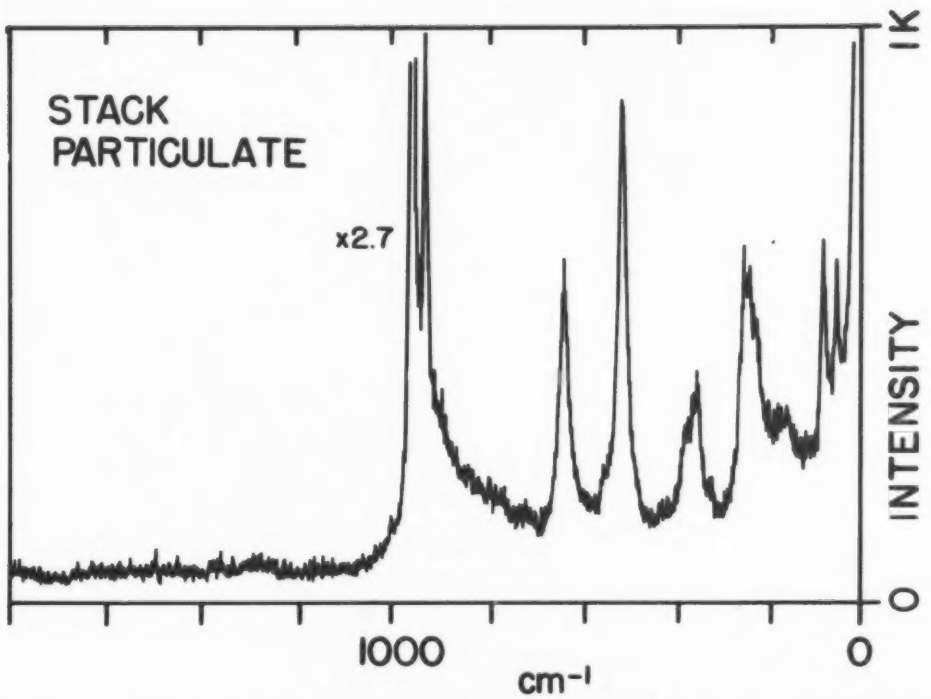


Figure 10. Raman spectrum of particle from an oil-fired power plant identified by indexed electron diffraction patterns and elemental composition to be sodium vanadium alum, $NaV(SO_4)_2 \cdot 12H_2O$. Particle ∿ 15 x 18 μm, substrate, Al_2O_3; laser, 514.5 nm, power 18 mW at sample; beam, ∿ 8 μm diameter, spectral slit width, 3 cm^{-1}; time constant, 3.0s; scan rate, 0.33 cm^{-1}/s; full scale, 1000 counts.

Further work is necessary to fully characterize these samples. Of interest is the positive identification of the Raman spectra which we have tentatively associated with sodium vanadium sulfate and the determination of the source of ammonia observed in many of the samples.

SECTION 6

A COMPARISON OF THE MOLECULAR OPTICAL LASER EXAMINER (MOLE) WITH THE NBS RAMAN MICROPROBE

As part of the contractual agreement, a comparison of the capabilities of the NBS Raman microprobe and the Raman microprobe/microscope (MOLE), which is commercially available from Instruments S. A., was desired. The imaging capabilities of the MOLE are of special interest for their possible utilization in the component specific analysis of environmental particles by the EPA.

The Raman microprobe/microscope (MOLE) is based on instrumentation adapted to obtain Raman spectra of microsamples and images of microscopic features using a characteristic Raman frequency.(38-42) The basic configuration of the MOLE results from the coupling of a conventional light microscope, using both light and dark field illumination, to a scanning spectrometer/spectrograph. The spectrometer is capable of good separation of spectral features and is also capable of transmitting images over a wide spectral range. The detection system consists of two assemblies: a conventional photomultiplier tube used for the monochannel detector as a molecular microprobe (in much the same method as the NBS Raman microprobe) and a vidicon detector used for a multichannel optical analyzer as a molecular microscope.

As a Raman microprobe, the MOLE operates in much the same fashion as the NBS instrument and EPA samples which we have analyzed in the MOLE and which had previously been analyzed in the NBS instrument gave comparable spectra with good signal to background level characteristics. Analysis of the same materials in the MOLE when operated as a Raman microscope gave diffuse images and a poor discrimination against luminescent backgrounds that did not permit satisfactory imaging of major scattering species in these heterogeneous samples.

The results that we have obtained in a limited application of the MOLE point to the presently inadequate capabilities of the instrument for effective Raman imaging of microscopic features in samples with the complexity of those examined in this study. Work is underway at the optical spectroscopy laboratory of ISA to improve the operation of the Raman microscopic mode through the use of an image processor.

Preliminary results with such a system indicate a definite improvement in the imaging capabilities of the MOLE. The images from the vidicon detector are digitized and stored in a two-dimensional array. In the analysis of a heterogeneous sample, the Raman line image is first taken at a Raman

frequency corresponding to the scattering component of interest (e.g., integration at 144 cm^{-1} for the detection of V_2O_5); then the "background" scattering intensity, which may have a fluorescent component, is integrated and subtracted from the digitized image obtained in the analytical Raman line. This results in an enhancement of the Raman image over background radiation, thereby increasing the sensitivity of detection and providing better spatial resolution in the mapping of individual components of a heterogeneous sample. For many Raman scattering molecules present as the predominant components of solid phase material, a spatial resolution of $\sim$ 10 μm can be attained for many types of sample matrices.

A further comparison of the NBS Raman microprobe with the MOLE is planned and the results of this comparison along with our recommendations will be transmitted to the EPA at a later date.

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16. ABSTRACT

The application of Raman spectroscopy to the molecular characterization of individual particles from stationary sources is described. The NBS-developed Raman microprobe has been used to characterize microparticles of oil- and coal-fired power plant emissions and boiler samples collected and described by the Environmental Protection Agency. The samples were examined on an "as received" basis and the results reported do not take into account any sample modifications that may have occurred during sample collection.

Vanadium pentoxide, V_2O_5, is identified as a major component of the oil-fired samples. The presence of other vanadium-bearing materials such as sodium metavanadate, $NaVO_3$, and sodium vanadium sulfate, $NaV(SO_4)_2 \cdot 12H_2O$, is indicated. No vanadyl (VO^{2+}) compounds have been detected in these measurements. Other Raman spectra are indicative of crystalline sulfates. These sulfates are mostly complex double salts. Materials that have been identified include nickel ammonium sulfate, $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$, iron ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, sodium vanadium sulfate, $NaV(SO_4)_2 \cdot 12H_2O$, calcium sulfate, $CaSO_4 \cdot 2H_2O$ (gypsum), and ammonium sulfate, $(NH_4)_2SO_4$, which we believe to have formed from sulfuric acid upon reaction with ambient ammonia. Raman microprobe analyses of a number of dense agglomerations of largely submicrometer particles, from a sample collected by the EPA and described as coal fly ash, show no Raman spectral features to indicate a glassy material when the particles are first exposed to laser excitation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air pollution		13B
Electric power plants		10B
* Particles		07D
* Chemical analysis		14B
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